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Free Radical Mediated Cellulose Degradation during High Consistency Ozonation

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Abstract: A study was performed on the ozonation of cotton linters at high consistency, 40%, and pH3, in order to shed some light on the mechanism of degradation of cellulose during pulp bleaching. Ferryl ions (FeO^{2+}), produced in the reaction of O_3 with Fe(II), was used to initiate free radical chain reactions to investigate the relation between chain reactions and degradation. The degradation was evaluated by viscometry. The degradation of cellulose responded more strongly to the propagation than to the initiation of the chain reactions. Also, the results suggest that the reactions responsible for initiation do not in themselves contribute to the observed degradation. Complementary experiments were made on cellulose beads (<5% crystalline). In contrast to the results from the cotton linters, the degradation of cellulose beads appears to correspond directly to ferryl ion formation. In non-structured cellulose (cellulose beads), cellulose is highly accessible. The degradation is thus directly linked to the total amount of radical attack. In naturally structured cellulose (cotton linters) only cellulose at fibril surfaces is accessible and will react. A chemical attack of fast-reacting agents on surfaces in structured cellulose should thus not be highly efficient in lowering the average chain length. What distinguishes radical chain reaction degradation in this context is that the spreading chain reaction is governed by the time

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of each step in the reaction cycle. The explanation that best fits our results is that of a free radical chain reaction, where the propagation step is rapid, which also implies that degradation is concentrated to zones along fibrils or fibers.

Keywords: Cellulose degradation, cotton linters, ozone, Fe(II), ferryl ion, free radicals, viscosity

INTRODUCTION

TCF (totally chlorine free) bleaching of pulp is used as an alternative to chlorine bleaching in response to the demand for more environmentally friendly methods. A concern in pulp ozonation is that the delignification process is paralleled by degradation of the cellulose fiber, which is claimed to reduce the paper strength. Many studies have been devoted to this problem.^[1–5]

The degradation is generally ascribed to the formation of radicals. Lately, the influence of cellulose structure upon the apparent degradation has received more attention.^[6–9] The efficiency of a radical to degrade cellulose should depend on the ability of the radical to reach individual glucosidic units in the cellulose chains. In fibrils, which have a non-homogenous cellulose chain arrangement, access to the cellulose chains in the interior is restricted. The scope of this study was to investigate free radical mediated cellulose degradation as a function of both cellulose macrostructure and free radical reaction in terms of the ratio of chain initiation to chain propagation. The degradation was assessed using viscometry. The experiments were performed using cotton linters. The mechanism of cellulose degradation during Fe(II)-controlled ozonation was determined, and different manifestations of the free radical mediated cellulose degradation were investigated, evaluated, and discussed.

Model of the Experimental System

Figure 1 depicts the physical conditions in the experimental system for cotton linters. The cotton linters fibril is composed of a crystalline core, a paracrystalline phase, and an accessible fibril surface layer (8% of the glycosidic unit total).^[10,11] In this article accessibility is defined as the accessibility of cellulose to water. Fibrils are aggregated to bundles and the bundles form fibers. Not all of the fibril surfaces are necessarily accessible in these bundles. On the other hand, the accessible fraction of cellulose must be larger than or equal to the cellulose on the fiber surface.

From the point of view of one ideal fibril, an initiator introduced into the water phase is expected to act on the fibril surface, given that the water phase is confined to the outside of the fibril. By abstracting hydrogen from C-H bonds, the initiator will produce glycosidic radicals on the fibril surface. Figure 2 shows the suggested reaction scheme. The ferrous ion, adsorbed onto the cellulose, is oxidized to the ferryl ion by ozone. The ferryl ion will

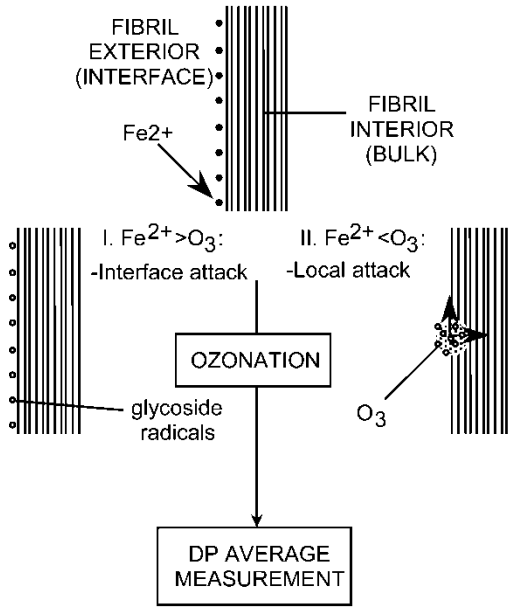


Figure 1. Experimental design. Hypothesis.

abstract hydrogen from the cellulose in the nearest proximity, forming glycosidic radicals.^[3-5] The carbon-centered radicals will be oxidized by oxygen to yield peroxy radicals. Additional ozone will affect cellulose degradation through a chain reaction mechanism; ozone will react with $O_2^- \cdot$ to form

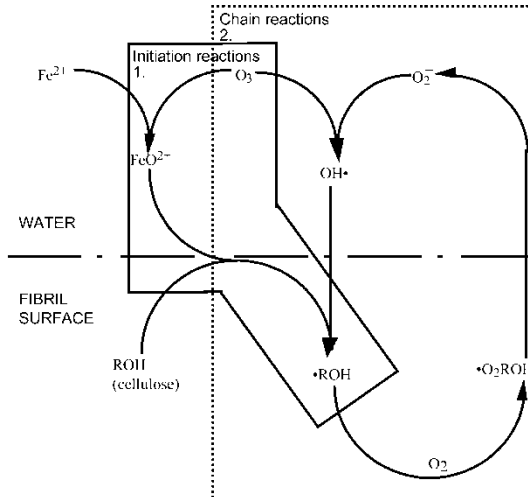


Figure 2. Principal reactions.

hydroxyl radicals, and the latter will react with cellulose to form new glycosidic radicals.^[12] Varying the charges of ferrous ions and ozone is a way to control the ratio of chain initiation to chain propagation.

The spatial spread of the radicals starting from the initial site is governed by the life times of the intermediates. The reactivity of the hydroxyl radical with carbohydrates and of superoxide with ozone should govern the degradation in the system.^[2] Based on reactivity, the hydroxyl radical should typically migrate 0.1 nm. The hydroperoxyl radical should migrate around 60 nm,^[13] which allows the radical sites to migrate, in-between reaction cycles, a distance that is longer than that for the hydroxyl radical but shorter than average cellulose chain lengths. Thus, the distance between radical sites that form in naturally structured cellulose during radical chain reactions will be short, in comparison to fibril and fiber length dimensions.

Oxidation of the glycosidic radicals results in cleavage of cellulose chains. Some scissions occur directly upon oxidation, whereas others can take place subsequently from oxidation products, such as those containing newly introduced carbonyl groups, as a result of elimination reactions during alkaline treatments. The locations of the radical sites during degradation will determine the location of scissions in the cellulose matrix, ultimately defining the distribution of chain lengths and the viscosity.

Two extremes were of interest in this work, namely, when either the ferrous ion or ozone is in excess. First, when ferrous ions are charged in excess of the ozone the ferrous ion will consume most of the ozone, leaving little ozone left to propagate the radical chain reactions. The degradation will be by way of the ferryl ion reactions at the fibril surfaces. Second, when ozone is charged in excess of the ferrous ions, the ozone will consume most of the ferrous ions and the ferryl ions will in turn abstract hydrogen at the fibril surface. Radical chain reactions will proceed in proportion to the amount of remaining ozone.

For comparison with the experiments made on the ozonation of cotton linters (cellulose organized in fibrils), experiments with less ordered cellulose were also made, using cellulose beads.^[14] Cellulose beads consist of dissolved cotton linters precipitated in water to form gels. Cellulose crystallinity in the beads has been studied by ¹³C-NMR and it is estimated to be <5%.^[15]

EXPERIMENTAL

Ozonation of Cotton Linters

The ozonation sequences will be described by two terms, AZE and AZRE. "A" refers to the acidic conditions employed, "Z" an ozone application, "E" an alkaline extraction stage and "R" the use of a reduction stage. The experiments were performed at pH 3. The pH was adjusted with aqueous sulfuric acid and sodium hydroxide at 1% consistency (wt) of the cotton linters. The

Fe(II) charge, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, was introduced at this point in an amount that corresponded to the desired amount at 40% consistency, assuming no adsorption. The pulp was equilibrated for 10–30 min, then pressed and fluffed to 40% consistency: A gas stream consisting of 1% ozone in oxygen was passed from an ozone generator, through a reactor (a rotary evaporator apparatus) and into an absorption flask that contained alkaline KI-solution. The KI-solution was titrated with sodium thiosulfate to measure the ozone content in the gas-stream in presence and absence of a cellulose sample. Cotton linters (10 g o.d. at 40% consistency) were ozonated in the rotating reactor at 20°C. The time of ozonation corresponded to the desired amount of ozone (40 mg or as otherwise specified). Ozone consumption was calculated as difference between the amount of ozone entering and leaving the reactor. The reduction stage (R) consisted of 0.1 g sodium borohydride/g (o.d.) cotton linters added to the linters at 1% consistency, which then was left over night. The alkaline extraction stage (E) was performed at 10% consistency with the pH adjusted to 12.0. The suspension was held at 60°C for 1 h and then washed until the pH was neutral.

Buckeye Ltd. supplied the cotton linters; DP 5200, viscosity 1500 mL/g, viscosities were determined according to the standard SCAN procedure.^[16]

The viscosity and ozone consumption data for the cotton linters experiments are presented in Table 1.

Table 1. Ozonation of cotton linters at 40% consistency and pH3. Change of the viscosity in response to the ozone and Fe(II) charges

Initial charges		Viscosity AZR mL/g	Viscosity AZRE mL/g	O ₃ Consumption O ₃ (out)/O ₃ (in) moles/moles
Fe(II) moles	Ozone moles			
1.0E-03	1.0E-02	476	326	
1.0E-03	1.0E-03	1353	1262	
1.0E-03	1.0E-03	1112	1333	
1.0E-03	8.3E-04	1169	802	
1.0E-03	1.0E-04	1507	1454	
1.0E-03	1.0E-04	1542	1447	
1.0E-03	1.0E-05	1518	1513	
1.0E-03	1.0E-06	1510	1505	
1.0E-02	8.3E-04	1493	1463	<0.07
1.0E-03	8.3E-04	1013	726	0.26
1.0E-04	8.3E-04	1001	683	0.69
1.0E-05	8.3E-04	1156	811	0.98
1.0E-06	8.3E-04	1266	955	1.01
—	8.3E-04	1225	863	1.02
—	8.3E-04	1224	846	
—	—	1542	1490	

Ozonation of Cellulose Beads

The beads were made from cotton linters with a typical consistency of 0.3–0.5% weight.^[14] The experiments were performed as a factor assay, where the factors were charges of O₃ and FeSO₄*7H₂O at pH 5. The iron and ozone charges were varied around a reference charge of 0.42 mmoles/g bead each (2 mg O₃/g bead). Cellulose beads (4 g in 60 mL MilliQ-water, 18.6 MΩ/cm) were used in the experiments. The iron was introduced as an aqueous solution at pH 4 (H₂SO₄) immediately before ozonation. After ozonation, 20 mL of 0.01 M NaOH was added and the sample was kept at 60°C for 1 h. The beads were washed with water until the pH was neutral. The viscosity-average molecular weight was determined by size exclusion chromatography (SEC).^[17]

The SEC data for the cellulose bead experiments are presented in Table 2.

Calculations

The degree of polymerization (DP) of the cellulose and the number of scissions per cellulose chain (random scission generation) was estimated through the following equations, which are valid for DP > 950.^[16]

$$DP = \left(\frac{\eta}{2.28} \right)^{1/0.76}; \quad n = \frac{DP_{\text{init}}}{DP_{\text{final}}} - 1$$

where η is the viscosity (mL/g) of the pulp, n is the number of scissions, DP_{init} is the DP before and DP_{final} is the DP after ozonation.

Table 2. Ozonation of cellulose beads at 0.3–0.5% consistency. Change of the viscosity-average molecular weight (SEC) in response to the ozone and Fe(II) charges

Initial charges		SEC
Fe(II) moles	Ozone moles	MW g/moles
2.1E–05	8.3E–05	1247000
4.2E–05	4.2E–05	1117000
8.3E–05	2.1E–05	1260000
8.3E–05	2.1E–05	1258000
4.2E–05	4.2E–05	1117000
2.1E–05	2.1E–05	1307000
8.3E–05	8.3E–05	981000
—	—	1398000
—	—	1398000

Direct scissions (ds) are the number of scissions calculated from the viscosities of the cotton linters treated by AZR. Alkali induced scissions (als) is a measure of the additional degradation from treating the sample with alkali and heat. The alkali-induced scissions (als) were obtained from a combination of ds and the number of scissions calculated from viscosities of cotton linters treated by AZE:

$$ds = \frac{DP_{init,ARE}}{DP_{final,AZRE}} - 1 \quad ts = \frac{DP_{init,AE}}{DP_{final,AZE}} - 1 \quad als = ts - ds$$

where ts denotes the total number of scissions.

RESULTS

Figure 3 shows the degree of direct scissions of cotton linters at different ozone charges but at a constant ferrous ion charge. The degradation was negligible unless O_3 was charged in excess of the iron ($Fe(II) = 1$ mmole). A charge of 10 mmoles of O_3 and 1 mmole of $Fe(II)$ resulted in substantial degradation. When charging 1 mmole O_3 , the degradation was similar to what was obtained when ozone was charged to cotton linters in the absence Fe^{2+} . In the experimental series of Figure 3, no degradation was observed unless ozone was present in the exit gas stream. An ozone outflow was detectable when the ozone charge was ≥ 1 mmole. The degradation increased with increasing ozone outflow.

The degradation from various iron charges at a constant ozone charge is shown in Figure 4. Figure 4 shows that intermediate amounts of Fe^{2+} , 10^{-4} – 10^{-6} moles of Fe^{2+} , increased degradation. This is consistent with the degra-

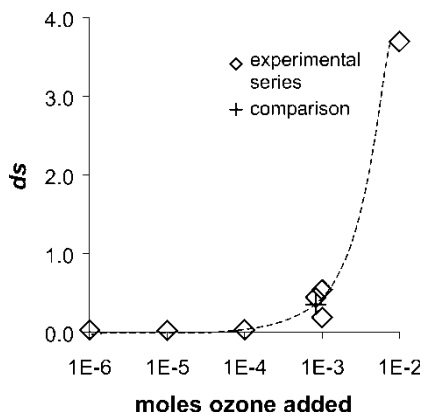


Figure 3. Degradation of cotton linters at high consistency, pH 3, $Fe(II)$ charge constant at 1 mmole, but varying the ozone charge. Comparison “+”: 8.3×10^{-4} moles O_3 , no $Fe(II)$ added.

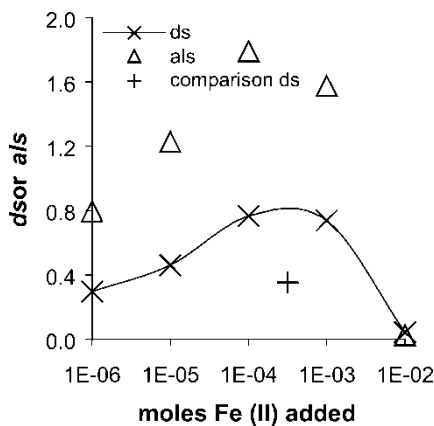


Figure 4. Degradation of cotton linters at high consistency, pH 3. Constant O_3 charge at 8.3×10^{-4} moles, but varying the Fe(II) charge. Comparison “+”: 8.3×10^{-4} moles O_3 , no Fe(II) added.

dation that occurred when O_3 was in excess of Fe^{2+} , which was observed in the interval ≥ 1 mmole in Figure 3. There was a maximum degradation, which is interpolated to occur when *ca.* 3×10^{-4} moles Fe^{2+} was added. In the presence of 10^{-3} moles Fe^{2+} or 10^{-6} moles Fe^{2+} , the degradation was similar to the case when only ozone was charged to cotton linters.

Figure 5 describes ozone consumption indirectly by way of the fraction of the ozone leaving the reactor at constant ozone charge but at different iron charges. That minor amounts of ozone may cause considerable cellulose

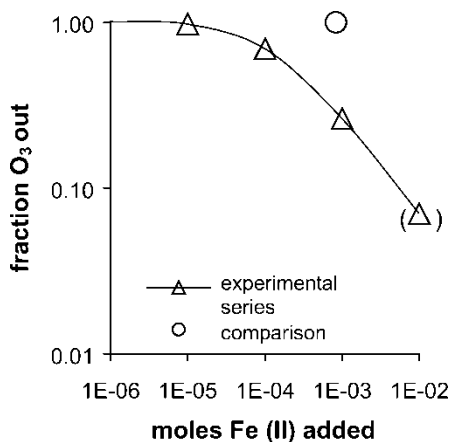


Figure 5. Fraction of ozone leaving the reactor during conditions as in Figure 3. The parenthetical point is the detection limit.

degradation can be concluded from comparing Figure 5 to Figure 4 in the 10^{-6} – 10^{-4} moles of Fe(II) interval. We also see that 1.6 mmoles Fe(II) and zero degradation of cellulose chains coincide in Figures 4 and 5. This is in agreement with the fact that a total consumption of ozone with a ferrous ion charge twice the ozone charge leads to the inhibition of chain reactions (potentially observable) and that to the extent ferryl ions do react with cellulose at these conditions, the degradation is not observable.

As seen in Figure 6 for cellulose beads, degradation was maximum when O_3 and Fe^{2+} were charged in 1 : 1 ratio in a series, where molar ratios of the reactants were 0.5 : 2, 1 : 1, and 2 : 0.5. Degradation was limited by the least charged reactant. The response was similar irrespective of whether O_3 or Fe^{2+} was in excess. The scission yield increased with the logarithm of the charge when the reactants were charged in equal amounts: the lowest at 0.5 to 0.5, increasing at 1 to 1 and the highest at a 2 to 2 charge (Figure 7).

DISCUSSION

Identification of Degradation Mechanisms

Cellulose in cellulose beads behaves differently from cotton linters in the O_3 – Fe^{2+} -system. The data in Figures 6 and 7, for bead reactions, are consistent with the degrading species being the ferryl ions formed in the reaction of ozone with ferrous ions. The FeO^{2+} yield should be optimal at a reactant ratio of 1. Furthermore, the yield of ferryl ion should depend similarly on both reactants and should be limited by the reactant with the lowest charge.

No effects from radical chain reactions or from direct ozone attack could be seen in the cellulose bead experiments. Data are insufficient for conclusive

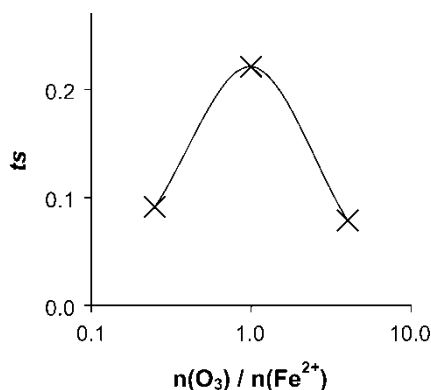


Figure 6. Ozonation of cellulose beads, pH 5. Constant 0.4 mmoles reactant added per g cellulose beads, but varying the molar ratio of O_3 to Fe^{2+} .

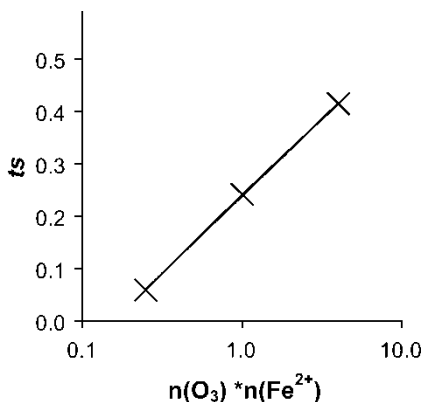


Figure 7. Ozonation of cellulose beads, pH 5. Fixed molar ratio, 1 : 1 of O_3 to Fe^{2+} , but varying the amount of reactants at 0.2, 0.4, and 0.8 mmoles of each per g of cellulose beads.

explanations. The observed strong cellulose bead degradation by the ferryl ion is indicative of the existence of an initial complex between $\text{Fe}(\text{II})$ and the cellulose. The ferryl ion is formed in close proximity to the polymer chain and its fast reaction with the polymer should be favored. Chain reactions, on the other hand, do not benefit from complexation. In addition, the radicals involved will be dissolved in a larger water volume than in the experiments with structured cellulose. Both of these factors serve to decrease the role of chain reaction degradation in cellulose beads. As for direct ozone attack, its reaction rate is by far smaller than that of ferryl ion formation and should hence be disfavored.

In structured cellulose (cotton linters), the degradation mechanism appears complex. First, it is necessary to determine whether the reaction between ferryl ions and cellulose actually is detectable. Degradation increased with the addition of iron in the interval 10^{-6} – 10^{-4} moles of $\text{Fe}(\text{II})$ (see Figure 4). This suggests that iron and ozone must form a degrading intermediate. The potential degrading agent should be a hydrogen-abstracting radical. To degrade cellulose, the glycosidic radical that forms must, in the next step, be oxidized by O_2 . We conclude that at least some ferryl ions must reach and react with it. The observed degradation then depends on either ferryl ions solely or in combination with chain reactions.

Secondly, we address the homogeneity of degradation. In Figure 4, at the higher concentrations side of the maximum (i.e., 10^{-4} – 10^{-2} moles $\text{Fe}(\text{II})$), the ozone available for propagation of the radical chain reaction will be limited, as the ozone is consumed by ferrous ions to form ferryl ions. If the ferrous ions were homogeneously distributed in the cotton, we would expect, in analogy with the cellulose beads, an increase in ferryl ion formation to be paralleled by an increase in the ozone consumption and degradation.

Comparing Figures 4 and 5 in this interval, we observe that the ozone consumption increased although the degradation decreased. Thus, we conclude that the ferryl ions were not homogeneously distributed because of the cellulose structure. Also, at concentrations of $\text{Fe(II)} > 5 \times 10^{-3}$ moles and with the Fe(II) only located at accessible cellulose, the distance between iron ions could be so short as to make Fe(IV) react with a neighboring Fe(II) to form two Fe(III) instead of reacting with cellulose. If so, the experimental point of 10^{-2} moles of Fe(II) in Figure 4 could be explained in terms of Fe(II) "protecting" cellulose.

Next we consider the question as to whether or not the observed degradation of cotton linters is only dependent on the direct attack of ferryl ions. Ozone was found to be completely consumed in its reaction with ferrous ions when less than 1 mmole of ozone was charged to samples of cotton linters containing 1 mmole Fe^{2+} or more. Thus with no ozone left for secondary reactions in this interval, the chain reaction should be inhibited and the remainder should be the effect of ferryl ions. As seen in Figure 3, degradation of cotton linters in this interval is almost independent of the addition of iron, in stark contrast to the findings for cotton beads. The reason might be that a relatively small amount of substrate is accessible to degradation in cotton linters. We thus conclude that, although degradation is likely to occur, the effect of direct degradation by ferryl ion attack is below detection and thus the reaction of ferryl ions reacting with glycosidic units is not a primary cause of the degradation. Data indicating a lesser impact from surface- than bulk-attack have been presented earlier.^[18,19]

Thus, the most likely degradation mechanism in structured cellulose is the ozone-driven free radical chain reaction. Here, the ferryl ion contributes indirectly as an initiator of the chain reactions.

Free Radical Chain Reactions and Structured Cellulose

On the low concentration side of the maximum in Figure 4, that is, with 10^{-6} – 10^{-4} moles Fe(II) added, the ozone charge is in excess of the ferrous ion charge. The increased degradation within this interval reflects the increase in the initiation rate due to ferryl ions. The increase is proportional to the initial Fe(II) charge raised to the power of 0.2. Ozone consumption at these conditions is marginal (cf Figures 4 and 5). As there was no appreciable depletion of ozone, we conclude that the amount of ozone that degrades the cellulose must be small in comparison with the ozone charge, illustrating the sensitivity of structured cellulose to the degrading agent.

Figure 3 illustrates that at 1 mmole of Fe(II) an increase in the ratio of $\text{O}_3/\text{Fe}^{2+}$ from 1 to 10 is paralleled by a large increase in the degradation of cellulose—much larger than what is observed on the left hand side of the maximum in Figure 4. In this region almost equal amounts of ferryl ions are formed in each experimental run. Thus, the initiation rate of the radical chain is constant and the increase has to be attributed to an increase in

chain length. The degrading response to Fe(IV) in itself is minor, as can be seen by comparing the Fe(II)-free reference point with the points containing 10^{-3} mol Fe(II) in Figure 3. Although somewhat more ozone is supplied in the latter case, no significant difference can be observed.

Evidence Supporting the Notion That Free Radical Chain Reactions Are Mainly Responsible for the Cellulose Degradation

In cellulose, oxidations at positions 1 and 4 of the glucosidic units are related to the *ds* value whereas oxidation at positions 2, 3, and 6 are related to the *als* value. The component immediately responsible for attack on cellulose during the radical chain reaction is likely the hydroxyl radical. The ratio of hydroxyl radical attack at positions 1 and 4 to positions 2, 3, and 6 of the glucosidic unit can be calculated to be about 0.4.^[20,21]

In Figure 4, the *ds* and *als* values were measured at a constant ozone charge. In the range of 10^{-6} – 10^{-4} moles Fe(II), the ozone concentration in the system is essentially constant. Being the result of the hydroxyl radical activity, both *als* and *ds* will increase with increasing iron charge—the *als* value being higher than the *ds* value by a constant factor. As seen in Figure 4, in this regime the ratio of *ds* to *als* is 0.4, in agreement with the predicted value. Interestingly, a similar *ds* to *als* ratio can be calculated from data collected during ozonation of oxygen bleached hemlock pulp.^[22,23]

When the Fe(II) charge is higher than the O₃ charge, the length of the radical chain is limited. As seen in Figure 4 the *als* to *ds* ratio approaches 1. The overall decrease in degradation should lead to a decrease in *als* and *ds*. When no degradation occurs at all, the *als* and *ds* values should be zero. Hence, the *als* to *ds* ratio should decrease to the limiting value of 1. This is in rough agreement with observation. Here, an increasing part of the reactions could stem from reactions not involving the hydroxyl radical. If these reactions participate in chain reactions and have a different selectivity toward cellulose than the hydroxyl radical, a change in the *als* to *ds* ratio would be expected.

In the experimental series “Fe constant” the total degradation was too low to offer any additional information on *als*.

Ozone Reacting with Cellulose

Cellulose with no additives degraded as if ppm-levels of transition metals had been added. This may be due either to (1) the presence transition metals in the original cotton linters or (2) the direct attack of ozone on cellulose that causes degradation.

Mass spectrometry (ICP-MS) of the “pure” cotton linters showed that 9 μ moles of Fe were present in 10 g of sample, which is in line with the

observed limit of 10^{-6} moles iron added. However, only a minor fraction of this iron can be assumed to be in the oxidation state +II. It is possible that the total of all transition metals in respective active states makes the level equivalent to 10^{-6} moles iron, or that the metals are concentrated locally in "hot spots".^[24]

Theoretically, the direct attack of ozone can be a source of initiation, depending on the ability of ozone to abstract hydrogen from carbon positions in the glycoside unit. Attack on the anomeric carbon has been suggested, but whether or not it is of radical or ionic character is a moot point.^[25,26] In support of this mechanism we have two arguments: (1) ozone seems able to abstract hydrogen directly from the α -carbon of alcohols and (2) *ds* to *als* ratios in the present systems are similar to those from ozonation of systems containing cotton linters or pulp with no transition metals added.^[13,23,27] The degradation from ozone reacting with cotton linters could therefore be explained by a slow initiation process that could be either from ozone abstracting hydrogen or a small initiator content in "pure" cotton linters.

Rationale of Experiments

When the physical organization of cellulose (structure) increases too much, the direct relationship between ferryl ion formation and cellulose degradation is lost. Instead effects of chain reactions become important. This indicates a synergism between the physical nature of the cellulose and free radical chain reactions.

In non-structured cellulose (cellulose beads), the cellulose is highly accessible. Logically speaking, the degradation is directly linked to the total amount of attack, irrespective of its origin. In naturally structured cellulose (cotton linters) only cellulose at fibril surfaces is accessible and will react. An attack of cellulose by reactive agents solely at the surfaces should not be highly efficient with respect to decreasing the average chain length. As for free radical chain reactions, the degradation could be confined to the accessible cellulose and degrade in a fashion similar to that caused by ferryl ions. If so, the propagation reactions should effect negligible viscometrical change in the cellulose. However, as it turns out, free radical chain reactions do cause detectable degradation.

Chain reactions are governed by a series of steps in a reaction cycle. The time of a cycle can modify the mechanism of cellulose degradation. The possibilities are delimited by the following two extremes: a short cycle time will concentrate the attack to the area close to the initial site, whereas a long cycle time allows infinite spreading as depicted in Figure 8. In cellulose, structure influences degradation in at least three ways: (1) by dissolution of fragmented cellulose to uncover inner cellulose, (2) by migration of dissolved substances, and (3) by hypothetical existence of amorphous micro-regions in the fibrils.

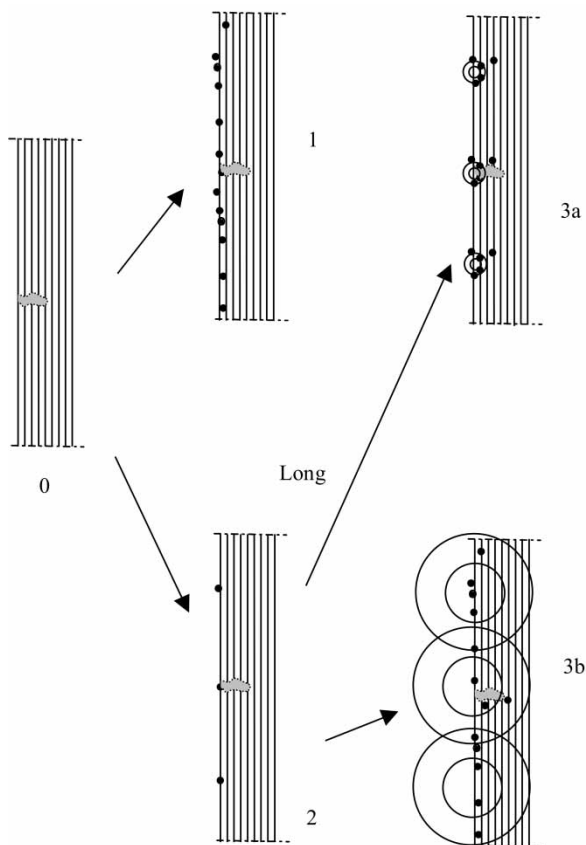


Figure 8. Different scission distributions. 0: Structured cellulose, 1: Surface attack, 2: Initiation of free radical chain reactions, 3a: Fast propagation of chain reactions, 3b: Slow propagation of chain reactions.

Many mechanistic combinations could be envisioned that might prove more efficient than a general surface attack. One example is that of degradation zones along fibrils or fibers, Figure 8-3a, caused by a relatively fast propagation step, which theoretically lead to locally concentrated degradation in the fibrils with only small, easily dissolved, fragments to remove. Such a mechanism would provide a way for the radical sites to work themselves into the fiber or fibril. Migration of the radical site into the core of the fiber would potentially make all of the cellulose chains subject to attack. A second example is a relatively slow propagation step in combination with the hypothetical existence of amorphous micro-regions in the fibrils, Figure 8-3b. This would enable the agents not only to spread but also to penetrate into the fiber.

The general implication of this work is that cellulose degradation by radicals produced during ozone bleaching need to be set into the perspective

of free radical chain reactions and cellulose physical structure to be understood. The common practice of explaining degradation by an unspecific reference to radicals, formed during bleaching, is inadequate. Formation of radicals does not become relevant to cellulose degradation unless these radicals are able to initiate chain reactions and there is ozone left to propagate the radical chain reactions. As the formation of radicals seems unavoidable, it is the excess of ozone that should be addressed in order to decrease degradation during ozone bleaching rather than the sources of initiation.

SUMMARY

Degradation from the free radical chain reactions that follow from the direct reaction between ferryl ions and cellulose was detectable using viscometry. Surface degradation, the direct reaction in itself, was not detectable. Propagation of chain reactions had a stronger effect than initiation. The results are best explained by degradation localized to zones along fibril or fibers. It was also noted that the *ds-als* ratio may be essentially constant and relate to the nonselective oxidation of different positions in the glycosidic and the subsequent reactions in alkaline environments.

Mechanisms of free radical chain reactions in cellulose are distinct from non-radical chemistry, and need to be addressed as such. Merely stating “hydroxyl radicals” or “free radicals” inadequately summarizes free radical mediated cellulose degradation.

The results, in the context of pulp bleaching, suggest that ozone in excess of the delignification demand should be addressed in order to decrease degradation during ozone bleaching rather than sources of initiation. Possible initiation sources in normal cellulosic materials during ozonation are native transition metal ions and direct reaction between ozone and cellulose.

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